

Effect of Fly Ash Washing Conditions on the Properties of Coupling Agent Modified Polypropylene/Fly Ash Composites

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Abstract – Two fly ash samples (one from UK, UKFA, and another one from South Africa, SAFA) were washed with water and 1 M hydrochloric acid (followed by water) prior to incorporation (at 65 % wt) into polypropylene homopolymer, containing an unsaturated carboxylic acid coupling agent (Lubrizol Solplus[®] C800) with dicumyl peroxide free radical initiator. Melt blending was achieved using a Haake Rheomix 600 mixing chamber and composite test plaques were compression moulded. Flexural and impact testing was then carried out. Unwashed and water washed fly ash based composites responded well to C800 modification and flow micro-calorimetry (FMC) and diffuse reflectance FTIR (DRIFTS) studies confirmed strong interaction between C800 and fly ash. However, washing the fly ash with HCl led to a reduction in composite flexural and impact properties. SEM imaging of the latter composite fracture surfaces revealed poor filler-matrix adhesion, which was thought to be due to reduced interaction between C800 and HCl washed fly ash. The latter was confirmed using flow micro-calorimetry. Reduction of C800 / fly ash interaction led to a reduction in the nucleation of PP crystallisation and a decrease in melt flow rate. The latter may be due to a shift in locus of PP – C800 addition reactions from the interfacial region to the bulk matrix.

INTRODUCTION

Fly ash is a residue that consists of fine spherical particles that are formed as a result of the combustion of coal in power stations. During coal combustion there are two by-products that are normally produced, i.e. CO₂ (gas) and fly ash (solid waste)¹. Landfill is becoming an increasingly less attractive choice for disposal of waste due to increasing amounts of tax imposed². Alternative uses for fly ash are therefore, being sought and have become a priority for its continued future use. Some alternative uses already explored are as a filler in polymeric materials^{3,4}, as a replacement of clay in bricks⁵, in road pavements⁶ or in waste management⁷.

The addition of filler in polymers and polyolefin blends increases stiffness, but normally at high filler levels it reduces strength and toughness. This fact is normally due to a poor dispersion of the filler and weak polymer-filler interactions. Surface modification of the filler (i.e. coupling agents) is often required to improve the interfacial properties and hence filler dispersion and matrix-filler interaction

As indicated before, the interfacial region of the fly ash-polymer composites can be improved by coupling agents. Iraola-Arregui et al.⁸ assessed the performance of different coupling agents in PP-fly ash composites in order to find the most suitable coupling agent for such composites in terms of strength-toughness balance. Lubrizol Solplus[®] C800 coupling agent was found to give the best strength-toughness balance.

A number of studies have been reported in these last few years exploring the use of fly ash as filler for polymeric matrices. Deb Nath et al.⁹ found interesting crystallization results in the DSC analysis when correlating the existence of fly ash particles to β -nucleation of an isotactic polypropylene. Furthermore, OH groups on the fly ash surface may be responsible for interaction with PP chains, or more likely PP chains featuring carbonyl species. Atikler et al.¹⁰ analysed the mechanical and morphological properties of calcium carbonate and fly ash filled HDPE composites after 3-aminopropyltriethoxysilane treatment, and found that it led to significant improvements in mechanical behaviour. Bose & Mahanwar¹¹ also investigated the effect of fly ash filled nylon 6 with a tetraisopropyltitanate coupling agent, which resulted in increases in tensile strength, impact strength and heat distortion temperature.

Based on the results obtained by Iraola-Arregui⁸ and a previous adsorption study of C800 on to fly ash particles¹², the effect of pre-treated fly ash (UK and South Africa sourced) will be investigated in a PP homopolymer matrix with DCP/C800 commercial coupling agent modification. The purpose of this work is to probe the interaction between fly ash and PP and determine which fly ash type gives a better response in PP based composites. A further aim of the investigation was also to assess whether fly ash-PP composite materials with acceptable physical and mechanical properties could be produced for low cost applications thereof.

EXPERIMENTAL SECTION

Materials

Two different types of fly ash were used for the study.

- Mintron 7 fly ash, supplied by Rocktron Limited, Bristol, UK (coded UKFA, with an average particle diameter of 3.1 μm and an aqueous slurry pH of 9.3).
- Superfine SuperPozz fly ash, supplied by Ash Resources, South Africa (coded SAFA, with an average particle diameter of 3.2 μm and an aqueous slurry pH of 10.4).

Lubrizol Solplus® C800 (C800) coupling agent was used in this investigation. Its structure is shown in **Scheme 1** (please note that because the structure is proprietary, only a schematic structure, showing the key parts of the molecule, is provided).

C800 is an unsaturated carboxylic acid liquid type coupling agent manufactured by Lubrizol Advanced Materials, Inc. (UK). It was supported 50% wt on silica to give a more easily manageable powder. This form is named Solplus® C825. The effectiveness of C800 lies in the formation of a carboxylate linkage with basic filler surfaces together with its active double bond, which can interact with matrix macro-radicals. For avoidance of doubt the term C800 will be used in this paper to denote Solplus C825 as C800 is the active ingredient.

Dicumyl peroxide (DCP) was used as initiator for C825. This organic peroxide, named Akzo-Nobel Perkadox BC-40B, is 40% wt active using calcium carbonate as carrier.

The polypropylene homopolymer (PPH) was Borealis HD120MO with a melt-flow rate (MFR) of 8 dg min⁻¹ (230 °C, 2.16 kg) and a density of 908 kg m⁻³. It is understood that it contains a purpose stabiliser package.

Water and hydrochloric acid treatment of fly ash

This treatment was carried out in order to remove soluble ions from the fly ash surface. This will enable the effect of loss of certain elements on the adsorption of C800 and hence composite properties to be investigated. It was envisaged that HCl would be more aggressive at removing ions than water.

Fly ash (300.0 g) was added to deionised water (1.0 L) or HCl (1.0 M, 1.0 L) depending on the ion removal treatment. The suspension/slurry was stirred for 30 minutes using a magnetic stirrer. The fly ash was then isolated using Buchner filtration. The filter cake was washed with deionised water (5 x 0.2 L) before drying in an oven at 110 °C for 3 hours. The water and HCl washings were analysed using ICP-OES to establish which elements had been removed. The fly ash filter cake was micronized twice using a Waring blender fitted with a stainless steel chamber.

Adsorption study of C800 coupling agent on to fly ash surface

The adsorption of C800 onto washed and unwashed fly ash types (UKFA and SAFA) was studied at ambient temperature in heptane using flow micro-calorimetry and a solution adsorption studies.

Solution adsorption studies. Fly ash (5 g) was dispersed in heptane (50 mL) and the adsorbant (10 % fly ash mass, 0.5 g C800) was added to the mixture and agitated for 60 minutes using a magnetic stirrer. The C800 treated fly ash was then isolated by Buchner filtration, making sure the filter cake was washed on the funnel with a copious amount of heptane (5 x 50 mL) in order to ensure complete removal of

unreacted C800. The amount of C800 strongly adsorbed to the fly ash was determined by mass loss on ignition at 800 °C taking account of any water loss.

FMC study. The heats of adsorption and desorption of C800 on to the fly ash samples from heptane (dried over 3A molecular sieves) were determined using a Microscal 3V (partially converted to the all PTFE fluid path “i” specification). The principle run conditions were: sample mass 0.XXg; flow rate X ml hr⁻¹ and C800 concentration 0.3 % w/v.

For both the FMC and solution adsorption studies the interaction between the fly ash samples was investigated by diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) using a Thermo-Nicolet NEXUS FTIR spectrometer fitted with a Spectra-Tech DRIFTS cell. Before the analysis, all fly ash samples were diluted to 5 % wt with finely ground KBr. The KBr was pre-ground using an agate pestle and mortar. All spectra (from 500 cm⁻¹ to 4000 cm⁻¹) were recorded from 164 scans with resolution set to 4 cm⁻¹.

Composite preparation

All composites were prepared using a Thermo Haake Rheomix 600 mixing bowl fitted to a Thermo Haake Polydrive dynamometer unit. The bowl was fitted with Banbury rotors.

PP and fly ash were mixed with Solplus® C800 coupling agent (0.6 g of C800 per 100 g filler) and DCP (5% on C800 mass)¹³ for 10 minutes at a set temperature of 180 °C with a rotor speed of 80 rpm according to the formulation given in **Table 1**. The Polydrive software generated graphs of mixing torque and melt temperature versus mixing time. Values of the mixing torque and melt temperature were recorded for each sample.

After removing the mixed sample from the Rheomix Chamber, the molten composites were squashed between two steel plates with the help of a lever press into a 4 mm thick preform patty for compression moulding. The compression moulding of the samples into 102 mm x 102 mm x 3 mm composite test sheets was carried out using a frame mould. Pressure was applied using a 50 tonne hydraulic press with

electrically heated platens set at 180 °C and a second 50 tonne press with water cooled platens (15 °C) for the cooling of the sample. Total moulding time at 180 °C was four minutes and cooling time was 5 minutes.

Melt Flow Rate (MFR)

The melt-flow rate (MFR) of the composites was determined using a Ray-Ran melt-flow indexer at 230 °C with a 2.16 kg load. Extruded cut offs obtained over appropriate time intervals were used to calculate MFR (dg min^{-1}) and volume melt flow-rate (VMFR, $\text{cm}^3 \text{min}^{-1}$) values. Five replicate tests were done for each composite sample and the average value calculated by taking the closest four results with a 95 % confidence level.

Flexural testing

Flexural tests (in three point bend) were carried out using a Hounsfield H10KS tensometer fitted with a 1000 N load cell. The span between sample supports was 51.2 mm (16 times the thickness of the sample) and crosshead speed was 10 mm/min. Each test was done at ambient temperature ($21 \text{ °C} \pm 1 \text{ °C}$). Six replicate tests were done for each composite, calculating the average value taking the closest five results with a confidence level of 95 %.

Charpy impact strength measurement

Test pieces (10 mm x 4 mm in cross section) were notched (45° angle, with 0.5 mm tip radius) on the 4 mm side, to a depth of 2 mm, using a broaching tool. Notched and un-notched Charpy impact strength of the composite test pieces was measured using a Zwick 5102 pendulum type impact testing machine, equipped with a 2 J striker and a 40 mm span between the sample supports.

Each test was carried out at ambient temperature ($21 \text{ °C} \pm 1 \text{ °C}$). Five replicate tests were done for each notched and un-notched composite sample, calculating the average value by taking the four closest results with a confidence level of 95 %.

Non-isothermal Differential Scanning Calorimetry (DSC) analysis

A Perkin Elmer DSC-7 was used to investigate the melting and crystallization behaviour of the different PP-fly ash composites. Dynamic DSC analysis was carried out using a heat-hold-cool-heat cycle in a nitrogen atmosphere. The following temperature programme was used.

- Heat from 20 °C to 220 °C at 20 °C/min.
- Hold at 220 °C for five minutes.
- Cool from 220 °C to 20 °C at 20 °C/min.
- Hold at 20 °C for one minute.
- Heat from 20 °C to 220 °C at 20 °C/min.

The crystalline content in each composite was determined by using the following equation (**Equation 1**).

$$X_c = \frac{\Delta H_{sample}}{\Delta H_o} \times \frac{1}{X_w} \times 100 \quad \text{Equation 1}$$

Where X_c is the crystalline content, ΔH_{sample} is the measured melting enthalpy of the PP composite, ΔH_o is the of enthalpy value of 100% crystalline Polymer and X_w is the weight fraction of the polymer in the composite. For isotactic PP in the α -crystal form ΔH_o is 209 J g⁻¹ whilst ΔH_o for isotactic PP in the β -crystal form is 168.5 J g⁻¹ ^{14,15} and 277 J g⁻¹ for PE¹⁶. The onset and peak melting and crystallization temperatures were recorded.

Scanning Electron Microscopy (SEM)

SEM images of the fly ash filled polymeric systems were obtained using a Jeol JSM 5600LV SEM fitted with an Oxford Instruments INCA Sight energy dispersive spectrometer EDX detector probe. The accelerating voltage was 10 kV. Each impact fracture surface was cut from the test piece and mounted on standard aluminium Cambridge type stubs using conductive carbon particle loaded double sided adhesive tape. All samples were sputter coated with a gold/palladium alloy using a Polaron E5100 coating unit.

RESULTS AND DISCUSSION

ICP-OES analysis of water / HCl fly ash washings

Table 2 displays the concentrations of the principle ions present in both UKFA and SAFA per unit mass of filler. It can be clearly seen that more ions were removed as a result of the HCl washing than H₂O washing. This fact is directly related to the fact that most ions tend to form stable chloride-compounds which are soluble in aqueous solutions. As predicted, most ions removed in the H₂O washing process belong to the first and the second groups of the periodic table (i.e. Ca, Mg and Na), even if some p elements concentrations have also been detected (i.e. S and Si). However, during the HCl washing process a greater quantity of ions was removed, basically transition metals and p type elements, most of them due to their chloride - compound forming ability.

The chemical composition of both fillers is different as they were taken from different sources. Calcium and aluminium appear in greater quantities in the case of SAFA together with other p type elements such as sulphur or phosphorous. The presence of some of these ions may affect the nucleation of polypropylene crystallization, leading to variations in the physical and mechanical performance of the final composite material. The latter will be discussed in subsequent sections.

FMC study adsorption of C800 on to fly ash

Table 3 shows the recorded heats of reaction for the different fly ash samples during the FMC analysis.

It is evident that that there is a striking difference in the C800 adsorption behaviour of these fly ash samples. The UKFA fly ash adsorption is much more energetic than that of the SAFA. Treatment of the fly ash with water and hydrochloric acid also brought some changes in the adsorption behaviour. Treatment with water had little effect on the adsorption activity of UKFA but almost tripled the activity of the SAFA. However, treatment with HCl had little effect on the adsorption activity of SAFA but reduced the adsorption activity of UKFA by a factor of almost

five. In all cases the heat of desorption is substantially less than the heat of adsorption, indicating that the C800 is strongly retained on the fly ash surfaces.

Treatment of the fly ash with water and particularly HCl removes certain ions from the surface. These treatments will generally reduce the surface concentration of adsorption sites and therefore reduce adsorption activity. For this reason, there is a logical decrease in the heat of adsorption values recorded for the different UKFA samples. As expected, the greatest reduction occurred in the case of the HCl washed sample.

However, SAFA shows a different behaviour. The highest adsorption value was obtained for the H₂O washed sample instead of for the unwashed one. The temperature used during the analysis may have an effect on the adsorption of C800 coupling agent on to the filler.

DRIFTS analysis

The terminal acid group of C800 can chemically react with basic sites on the C800 surface via an ion pair interaction between the carboxylate group of the C800 and a metal ion on the fly ash surface¹¹ (**Scheme 2**). In FTIR spectra a change from a carboxylic acid to a carboxylate will be manifested as reduction in frequency of the carbonyl stretching vibration from ca. 1700 cm⁻¹ to ca. 1590 cm⁻¹¹⁸.

Figure 1 shows stacked FTIR spectra (from 2100 cm⁻¹ to 1000 cm⁻¹) of the pristine UKFA substrate, UKFA with adsorbed C800 and the substrate subtracted spectrum that emphasises the vibrations associated with interactions between the C800 and the fly ash surface. The spectrum of C800 is also shown in Figure 1. The oxides present on the fly ash surface give bands in the range of 1300-2000 cm⁻¹. These oxides belong to metallic ions (i.e. Al₂O₃), giving an Al-O stretching band at about 1650 cm⁻¹.

The spectra of C800 cannot be fully interpreted and understood as the exact molecular structure is proprietary. However, the main and most important groups can be deduced as follows¹⁷.

- The terminal carboxylic acid group can be recognized from three different peaks. The O-H vibration shows a wide band in the 3000 – 3500 cm⁻¹ region (not shown), while the two different C-O vibrations (carboxylic C=O and C-O ether) appear at 1710 cm⁻¹ and 1300 cm⁻¹ respectively.
- The alkenic double bond shows a vibration peak around 1600 cm⁻¹.
- The band at 3040 cm⁻¹ (not shown) is due to some alkenic C-H stretching vibrations.

The spectrum of the UKFA sample with adsorbed C800 shows some differences in relation to the pristine substrate. These differences are much better resolved by substrate subtraction. The appearance of a new peak at about 1590 cm⁻¹ is related to the carboxylate linkage with the metal from the filler surface, which confirms chemical adsorption of C800 onto fly ash. The carbonyl band at 1730 cm⁻¹ is assignable to an ester group present in the C800 structure.

Substrate subtracted spectra of unwashed, water washed and HCl washed UKFA and SAFA are shown in **Figure 2**. Considering both the UKFA and SAFA series in general terms first of all; it is strongly evident that UKFA adsorbed C800 more prolifically than SAFA, this observation supports the FMC data (Table 2) and the composite mechanical responses observed. Turning in detail to the UKFA series, it can be seen that water washing very slightly increased the level of adsorption whilst HCl washing nearly eliminated C800 adsorption – this observation is in direct agreement with the FMC data and composite mechanical responses. Interestingly unwashed SAFA showed very little strongly adsorbed C800, washing SAFA with water led to a noticeable increase in the amount of C800 adsorbed whilst HCl washing led to a decrease to a level similar to that for the unwashed sample. These changes are again consistent with the FMC data and composite mechanical responses.

Melt flow rate

Addition of fly ash to PP at 65 % wt resulted in the expected fall in MFR (**Table 4**), though the magnitude of the decrease was somewhat offset (relative to composites containing no C800/DCP) by DCP initiated chain scission reactions. Both SAFA and UKFA gave similar general trends in terms of the effect of washing

medium, though in both cases acid treatment resulted in reduced MFR, i.e. increased the viscosity of the composite melt. However, H₂O washed SAFA showed an unusually high VMFR value, this effect was investigated and was found to be repeatable. Further work is required to fully explain the origin of the effect though it was found that the water treated SAFA was shown using flow micro-calorimetry to have the strongest C800 adsorption activity of all the samples¹². It may be that prolific adsorption of C800 resulted in the coupling agent showing increased dispersant activity; filler – filler interactions may have been reduced to a greater extent, resulting in improved dispersion quality and reduced composite melt viscosity.

MFR and mixing torque data indicate that HCl washing of SAFA and UKFA resulted in increased composite melt viscosity, this was particularly noticeable with UKFA. FMC studies showed that HCl washing of fly ash reduced its interaction with C800, again the effect was most noticeable with UKFA¹². SEM imaging of fracture surfaces of composites based on HCl washed fly ash indicate poor filler-matrix adhesion (**Figure 3**). On first examination this observation appears counter-intuitive, however, previous work conducted by the fillers group^{8,13} has shown that shifting the locus of PP macro-radical addition to coupling agent molecules from the interfacial region to the bulk matrix can lead to an increase in composite melt viscosity. Removal of metal ions by HCl treatment reduced adsorption of C800 on to the fly ash, and may therefore have shifted the locus of macro-radical addition.

Mechanical properties

Flexural modulus trends (**Figures 4 and 5**) revealed no significant differences arising from varying washing conditions, though of course the expected stiffening effect of 65% wt filler addition was apparent. This is not too surprising bearing in mind the small strain at which flexural modulus is measured.

Unwashed UKFA performed better than unwashed SAFA in terms of composite flexural strength; in the former case flexural strength matched the maximum (yield) flexural strength of the unfilled matrix. This difference in behaviour may be due to the UKFA having a more porous surface (giving increased surface area) and stronger

surface area normalized interaction with C800¹². Strong interaction between C800 and fly ash will lead to more prolific coupling of PP chains to the filler surface and improved composite mechanical properties. Water washing of UKFA or SAFA led to a very slight reduction in flexural strength that was within the standard deviation for the data recorded and therefore cannot be regarded as significant. However, washing with HCl washing led to a significant reduction in tensile strength for both UKFA and SAFA based composites. This observation shows that removal of Mg²⁺ and Ca²⁺ ions from the fly ash surface by washing with HCl severely hampers its ability to interact with C800¹², resulting in much reduced coupling of PP chains to the fly ash and hence reduced filler-matrix interaction.

Predictably, addition of 65% wt fly ash reduced the deflection at break though the SAFA based composites suffered more in this respect due to the generally weaker interaction between SAFA and C800. Washing the fly ash with water made little difference, however, a more substantial reduction in deflection at break was observed for composites based on HCl washed fly ash due to the reduced filler-matrix interaction arising from reduced adsorption of C800.

Un-notched impact strength data is presented in **Figures 6 and 7**, considering the high filler level, the composites based on unwashed SAFA and UKFA perform similarly well. Washing the fly ash with water has no significant effect on composites based on UKFA but leads to a reduction in un-notched impact strength of composites based on SAFA. HCl washing leads to a significant reduction in un-notched impact strength, particularly with composites based on UKFA. The latter reduction is a further manifestation of reduced filler matrix adhesion arising from reduced interaction with C800¹².

The notched impact data reveals a significant decrease (roughly six-fold) for the unfilled matrix (relative to the un-notched value) and rather less significant reductions for the filled samples. Composites based on un-washed and water washed UKFA gave notched impact strengths higher than the unfilled matrix, a good result given the high filler level. Equivalent composites based on SAFA did not perform quite so well, average values of notched impact strength were slightly higher than the unfilled matrix, however, the increase was not outside the standard deviations obtained and is therefore not significant. Predictably, both HCl washed UKFA and

SAFA based composites performed poorly, with notched impact strength being similar to the unfilled matrix.

The impact strength data provides further evidence that the UKFA is the better of the two fly ashes examined; in notched impact tests the level of filler – matrix interaction gave an interphase structure that was conducive to improving toughness. The SAFA showed weaker interaction with C800 which manifested itself in weaker composites of reduced toughness. HCl washing was also highly detrimental to impact strength due to removal of C800 adsorption sites from the fly ash surface.

Non-isothermal Differential Scanning Calorimetry

The first heat data (not shown) revealed insignificant differences between the samples though in some cases (composites based on water and HCl washed UKFA) very small β -PP fusion peaks were evident. The α -polymorph was by far the dominant phase and crystalline content varied between 34 and 48 %. The PP matrix in composites based on HCl washed UKFA and SAFA had lower crystalline content, this was particularly true of that based on UKFA. Flow micro-calorimetry revealed that interaction of the latter with C800 was, in relative terms, reduced the most. Reduced interaction between the acid group of C800 and the fly ash surface will result in significant displacement of PP macro-radical addition to the C800 double bond from the interfacial region to the bulk matrix. Such an effect is likely to disrupt the structure of the PP chains via formation of what could be considered to be a branched random copolymer. The crystallization ability of such a material will be much reduced relative to the pristine PP. Reduced MFR of the composites based on HCl washed fly ash also supports a change in matrix structure arising from a shift in the locus of C800 – PP grafting reactions.

The cool from melt data revealed the most interesting observations, which may be related to the adsorption behaviour of C800 on to the various fly ash samples (**Table 5**). Equivalent composites based on the same fly ash sample but had not been modified with C800/DCP showed that whatever washing route, both SAFA and UKFA had almost no PP nucleation effects. Modification with C800/DCP enhanced the nucleation activity to varying degrees, depending on the nature of the washing

process employed. In the case of composites based on SAFA, water washing appeared to increase nucleation activity and also increased the strength of interaction with C800 (as measured by flow micro-calorimetry)¹², relative to the unwashed sample. However, washing with HCl reduced nucleation activity below that of the unwashed sample; the strength of interaction with C800 of HCl washed fly ash was also reduced relative to that for the unwashed sample. Similar trends were evident with UKFA though the nucleation activity was unaffected by water washing and was greater than that of the equivalent SAFA samples, this reflected stronger interaction of these samples with C800. HCl washing significantly reduced nucleation activity to a similar level to that attained with HCl washed SAFA. The latter observation is unequivocal evidence that the C800 related nucleation activity is directly related to its strength of interaction with the fly ash.

The second heat data was not particularly remarkable (and hence not shown). β -PP melting peaks were just discernible in composites based on HCl washed UKFA and unwashed SAFA. Crystalline content values from a second heat after controlled crystallization would be expected to be slightly greater than those obtained during the first heat as controlled crystallization would lead to more perfect crystal structures being formed. The latter was generally true for composites based on UKFA, however those based on SAFA tended to show a slight decrease in crystalline content in the second heat data. Considering the reduced overall interaction of SAFA with C800 this decrease may be related to further reactions with C800 occurring during the DSC analysis.

CONCLUSIONS

Composites based on UK produced fly ash (UKFA, Rocktron Mintron 7, added at 65 % wt) modified with the unsaturated carboxylic acid coupling agent, Lubrizol Solplus C800 (with dicumyl peroxide initiator), had better flexural and impact properties than equivalent composites based on the South African Superfine Super Pozz (SAFA) from Ash Resources. Water and hydrochloric acid washing (then drying) of the fly ash prior to addition to the composite was investigated. Water

washing had no significant effect on the flexural properties of the composites however washing with HCl led to a significant reduction in flexural and impact properties. SEM imaging of the fracture surfaces of the latter composites highlighted poor filler-matrix adhesion, whilst the composites based on unwashed and water washed fly ash showed strong filler-matrix adhesion.

It is significant that the melt flow rate of composites based on HCl washed fly ash were unexpectedly low, furthermore the α -PP crystal nucleation activity of HCl washed fly ash was also low. Flow micro-calorimetry revealed that UKFA interacted more prolifically with C800 than SAFA and that HCl washing reduced the amount of interaction between C800 and fly ash, this was particularly true for UKFA.

HCl washing of fly ash removed substantially more aluminium, calcium and magnesium than water washing. The latter are adsorption sites for the C800 acid group, and their removal therefore decreased interaction with C800. Such an effect reduced the effectiveness of C800 as a coupling agent but would not necessarily have prevented reactions between DCP initiated PP macro-radicals and the C=C bond of C800. Shifting of such addition reactions to the bulk matrix may have offset the effect of PP chain scission and have reduced the dispersant effect of C800, thereby resulting in a decrease in composite MFR. Lack of anchoring of PP chains to the fly ash surface, possibly together with inclusion of C800 into PP chains, will reduced PP nucleation activity.

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Figure Captions

Figure 1: DRIFTS spectra of C800, modified and unmodified unwashed UKFA and subtraction of both spectra at (a) 3800-2500 cm^{-1} and (b) 2100-1000 cm^{-1} regions

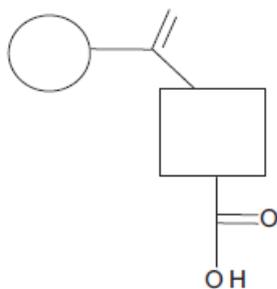
Figure 2: Subtraction spectra of washed and unwashed UKFA and SAFA fly ash compared with C800 at (a) 3800-2500 cm^{-1} and (b) 2100-1000 cm^{-1} regions

Figure 3: SEM images of fracture surfaces of C800/DCP modified PP-fly ash composites

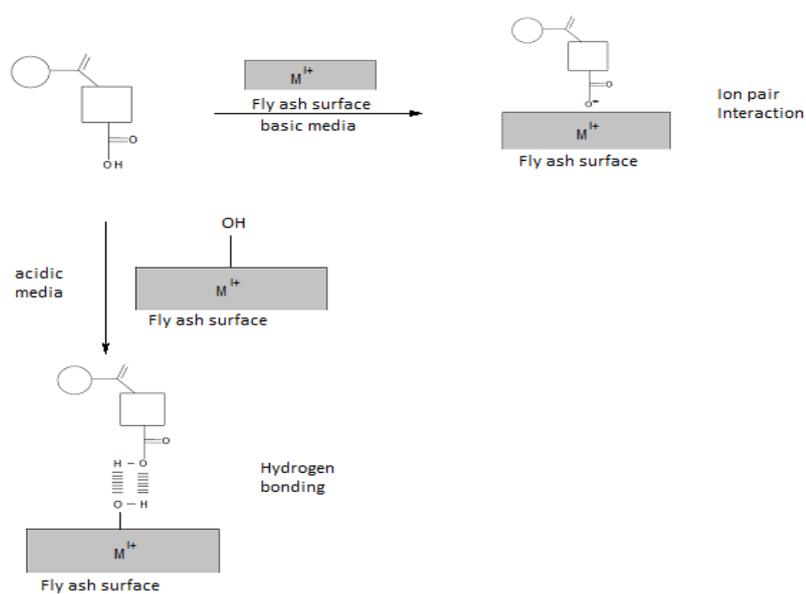
Figure 4: Flexural modulus, flexural strength maximum and deflection at maximum graphs for the different C800/DCP modified PP-fly ash composites

Figure 5: Impact strength graphs (notched and un-notched) for the different C800/DCP modified PP-fly ash composites

FIGURES, TABLES & SCHEMES



Scheme 1: Schematic molecular structure of Solplus® C800 coupling agent



Scheme 2: C800 – fly ash reaction diagram

Table 1: Formulation for 65 % wt fly ash filled modified composites

Fly ash (g)	Polypropylene (g)	C825 (g)	DCP (g)
56.9	30.6	0.6828	0.0427

Table 2: ICP data obtained for UKFA and SAFA under different leaching conditions

Element	Element concentration (mg/g filler)			
	Aqueous leaching		Hydrochloric acid leaching	
	UKFA	SAFA	UKFA	SAFA
Al	-	-	1.47	2.46
Ca	0.35	0.64	1.01	1.35
Fe	-	-	0.77	0.61
Mg	0.04	0.01	0.10	0.10
Na	0.14	0.12	0.18	0.12
P	-	-	0.48	1.35
S	1.01	2.21	0.36	0.83
Si	0.01	0.01	0.23	0.22

-<0.01 mg/g filler

Table 3: Heats of reaction for washed and unwashed UKFA and SAFA samples

	$\Delta H_{\text{reaction}}$ (mJ m ⁻²)			
	UKFA		SAFA	
	Adsorption	Desorption	Adsorption	Desorption
Unwashed	-159.8	26.9	-28.7	8.3
H ₂ O washed	-125.3	0.3	-76.0	0.7
HCl washed	-32.6	2.2	-22.3	0.6

Table 4: Blending properties of the composites

Sample	VMFR (cm ³ .10min ⁻¹)
PP unfilled	20.6
PP-UKFA (unwashed)	7.4
PP-UKFA (H ₂ O)	6.7
PP-UKFA (HCl)	3.3
PP-SAFA (unwashed)	6.1
PP-SAFA (H ₂ O)	9.4
PP-SAFA (HCl)	3.5

Table 5: DSC data of the cooling stage for all C800/DCP modified PP-fly ash composites

Sample	Onset T (°C)	Peak T (°C)	Crystallization range (°C)	Crystallinity level (%)
PP (unfilled)	110.8	105.9	20.0	45.6
PP-UKFA (untreated)	125.8	121.3	13.0	42.3
PP-UKFA (H ₂ O)	126.2	121.9	8.0	47.3
PP-UKFA (HCl)	117.8	113.9	8.0	38.9
PP-SAFA (untreated)	120.2	115.9	9.0	39.3
PP-SAFA (H ₂ O)	123.2	119.3	8.0	41.5
PP-SAFA (HCl)	118.3	114.6	8.0	37.2

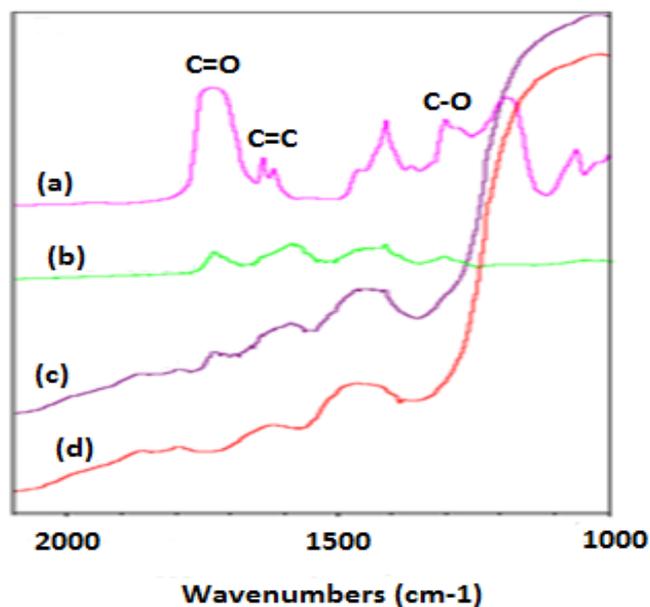


Figure 1: DRIFTS spectra of (a) C800, (b) subtraction, (c) modified and (d) unmodified unwashed UKFA at 2100-1000 cm⁻¹ region

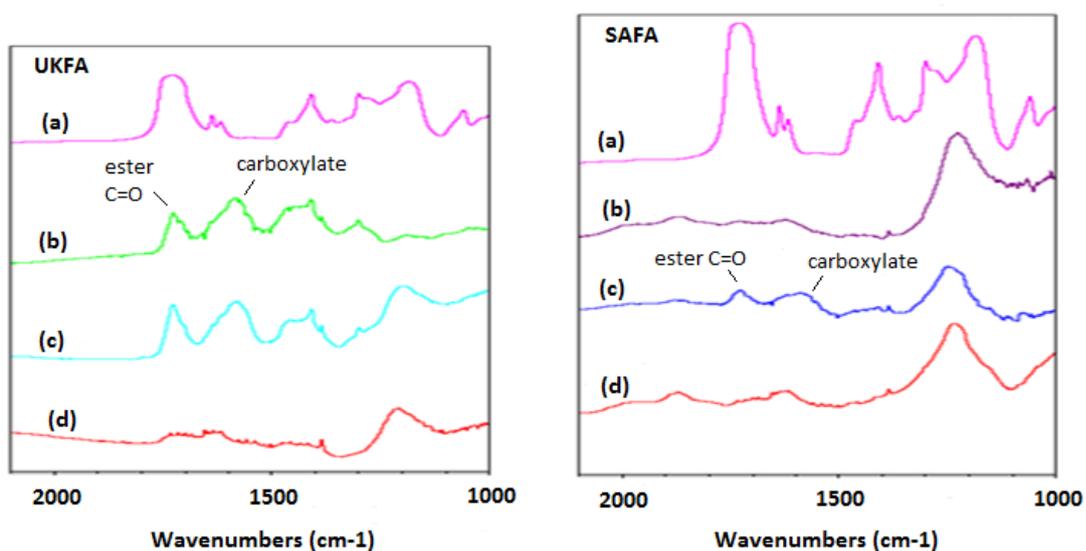


Figure 2: (a) C800 spectrum compared with (b) unwashed, (c) water washed and (d) HCl washed UKFA and SAFA subtraction spectra at 2100-1000 cm⁻¹ region

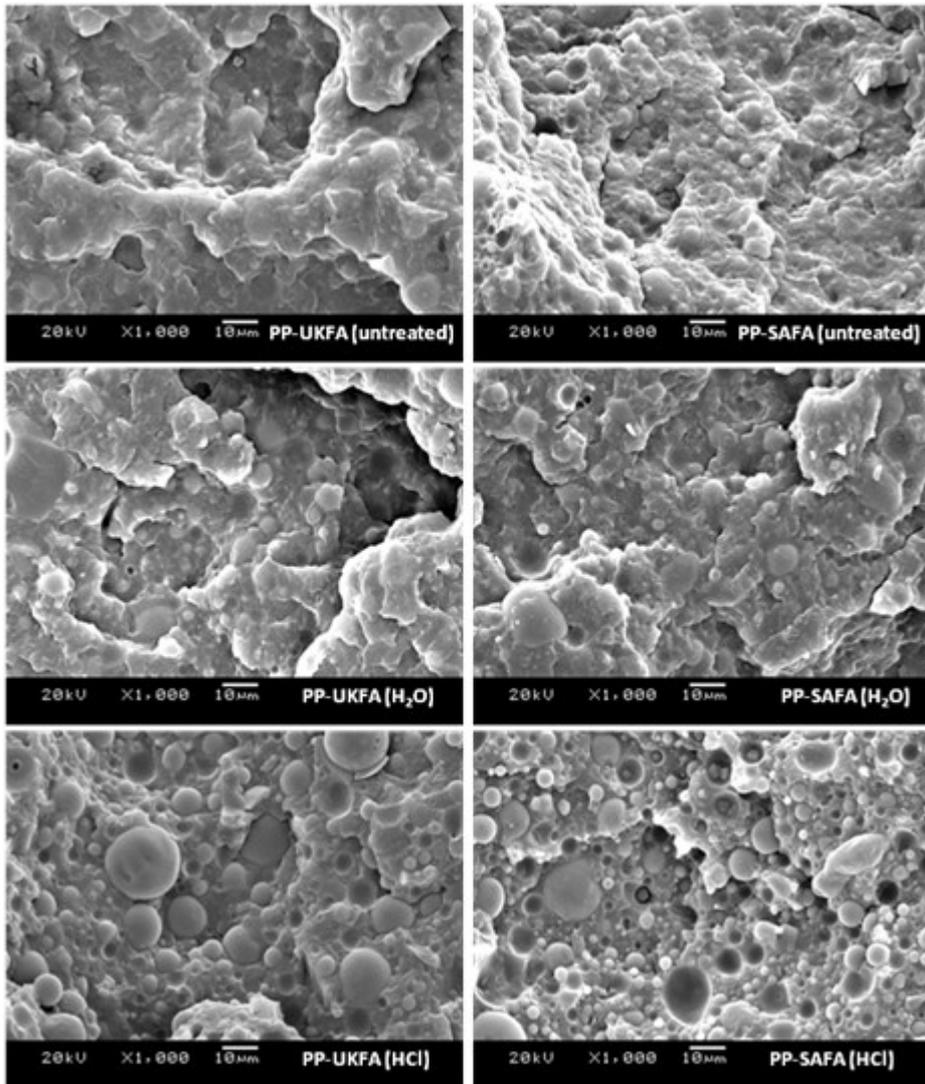


Figure 3: SEM images of fracture surfaces of C800/DCP modified PP-fly ash composites

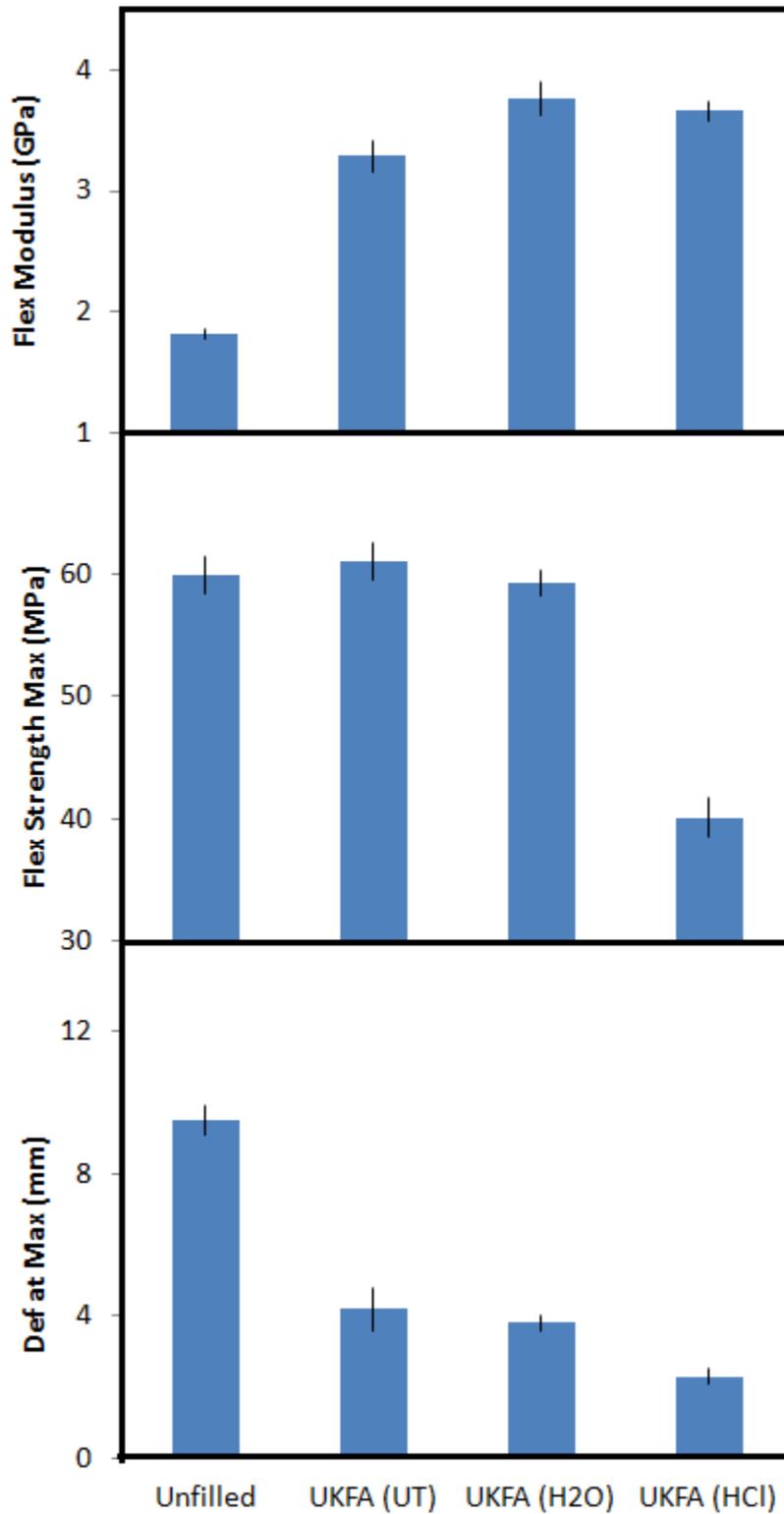


Figure 4: Flexural modulus, flexural strength maximum and deflection at maximum graphs for the different C800/DCP modified PP-UKFA composites

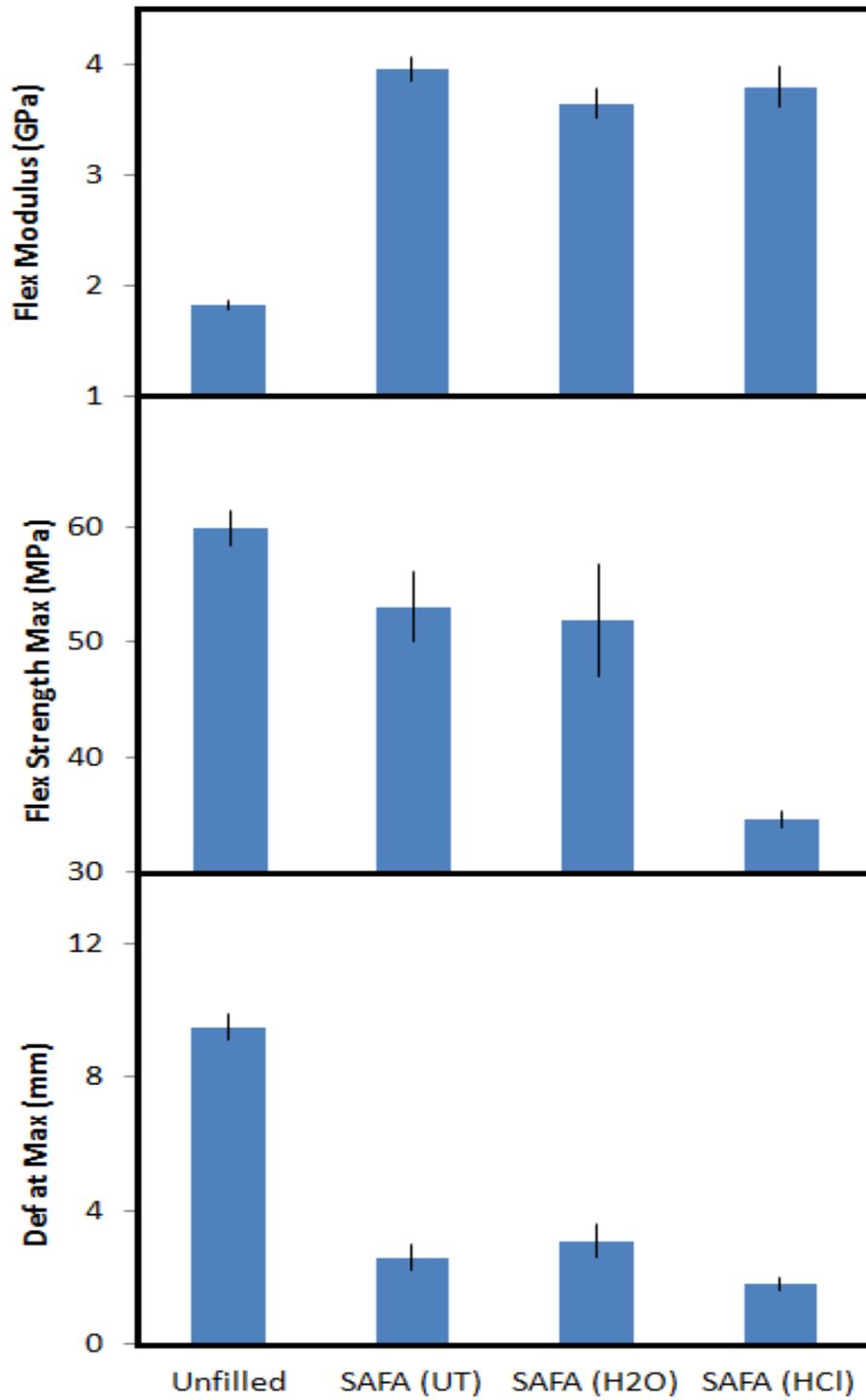


Figure 5: Flexural modulus, flexural strength maximum and deflection at maximum graphs for the different C800/DCP modified PP-SAFA composites

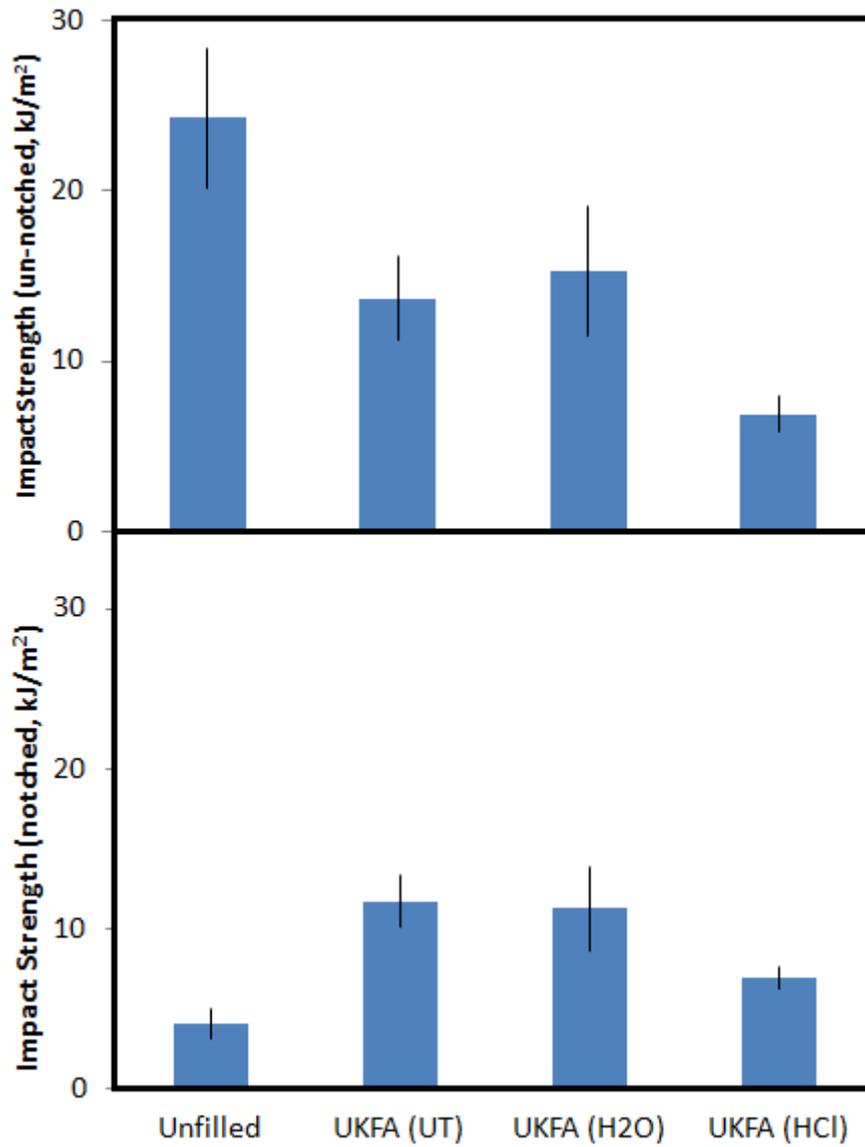


Figure 6: Impact strength graphs (notched and un-notched) for the different C800/DCP modified PP-UKFA composites

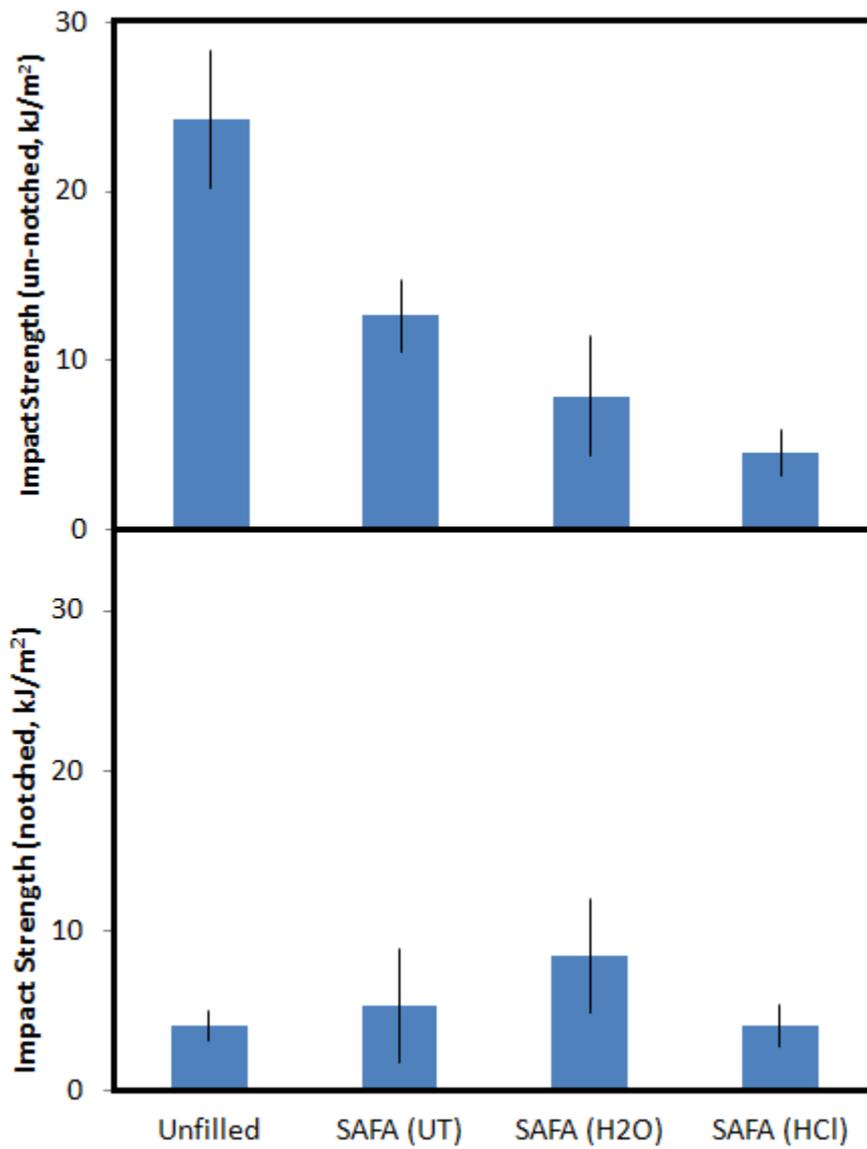


Figure 7: Impact strength graphs (notched and un-notched) for the different C800/DCP modified PP-SAFA composites

Text for the ‘Table of Contents’

A composite material of polypropylene and two different washed fly ashes were prepared, and their mechanical and physical properties evaluated. A coupling agent was employed to facilitate the incorporation of the fly ash in the polymer. It was found that stiffer composites were obtained, but that the bending and tensile strength decreased as a result of debonding between the filler and polymer matrix.

Graphic for the ‘Table of Contents’

